Electronic Supplementary Information (ESI)

Reversible stimuli-responsive luminescence of bimetallic cuprous complexes based on NH-deprotonated 3-(2′-pyridyl)pyrazole

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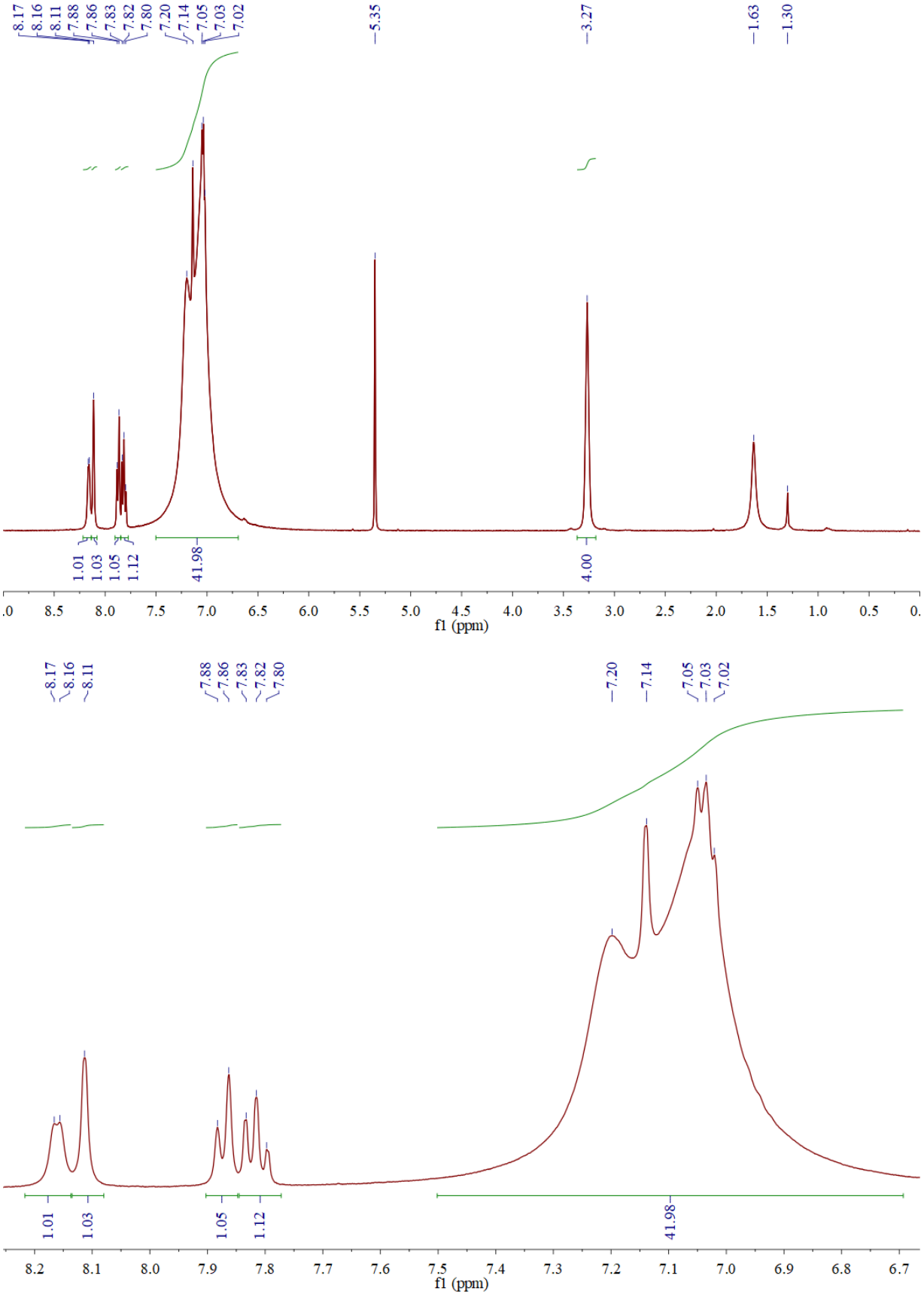

Fig. S1 ^{1}H NMR spectra of **1** in CD_2Cl_2.

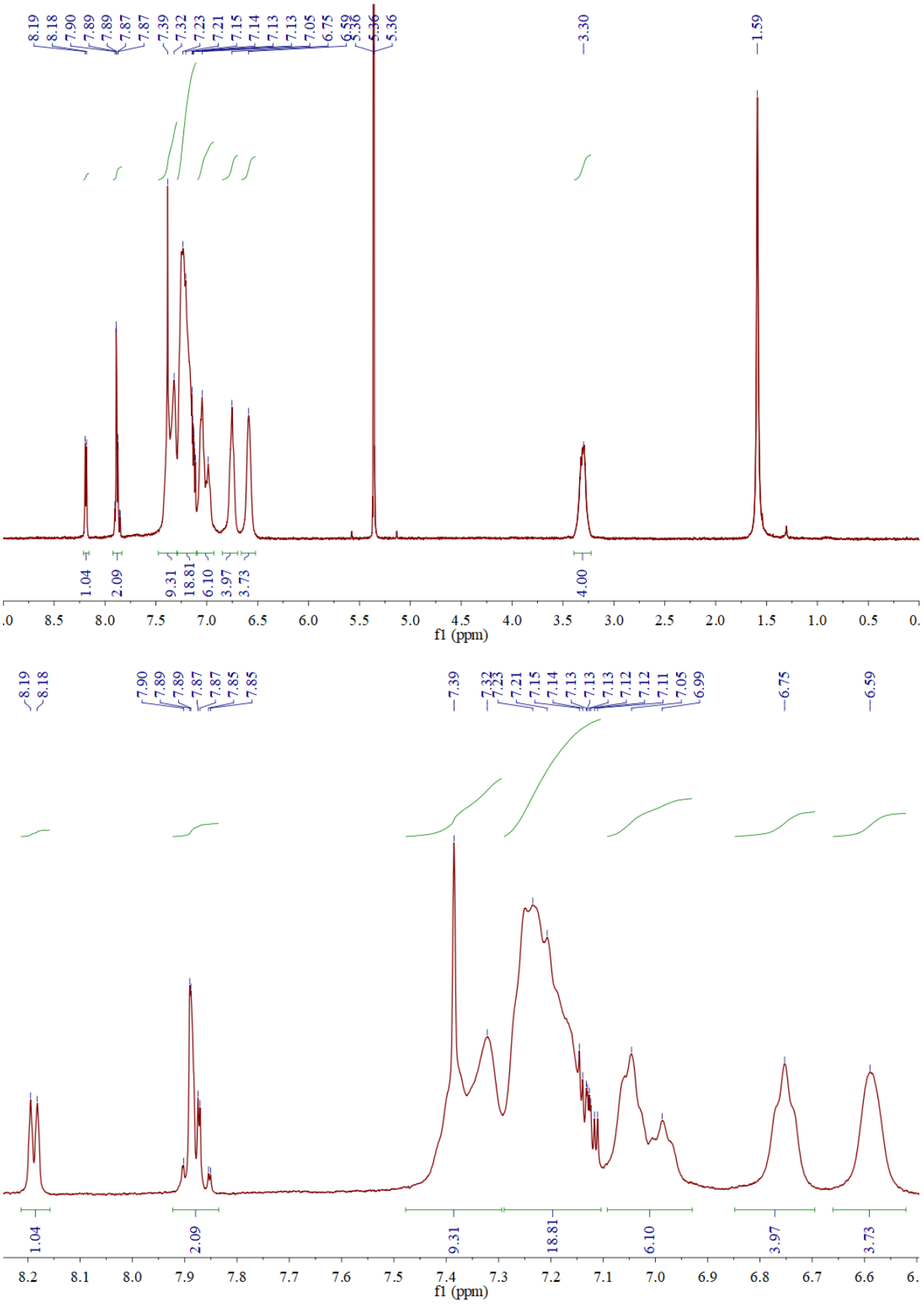

Fig. S2 ^{1}H NMR spectra of **2** in CD_2Cl_2.

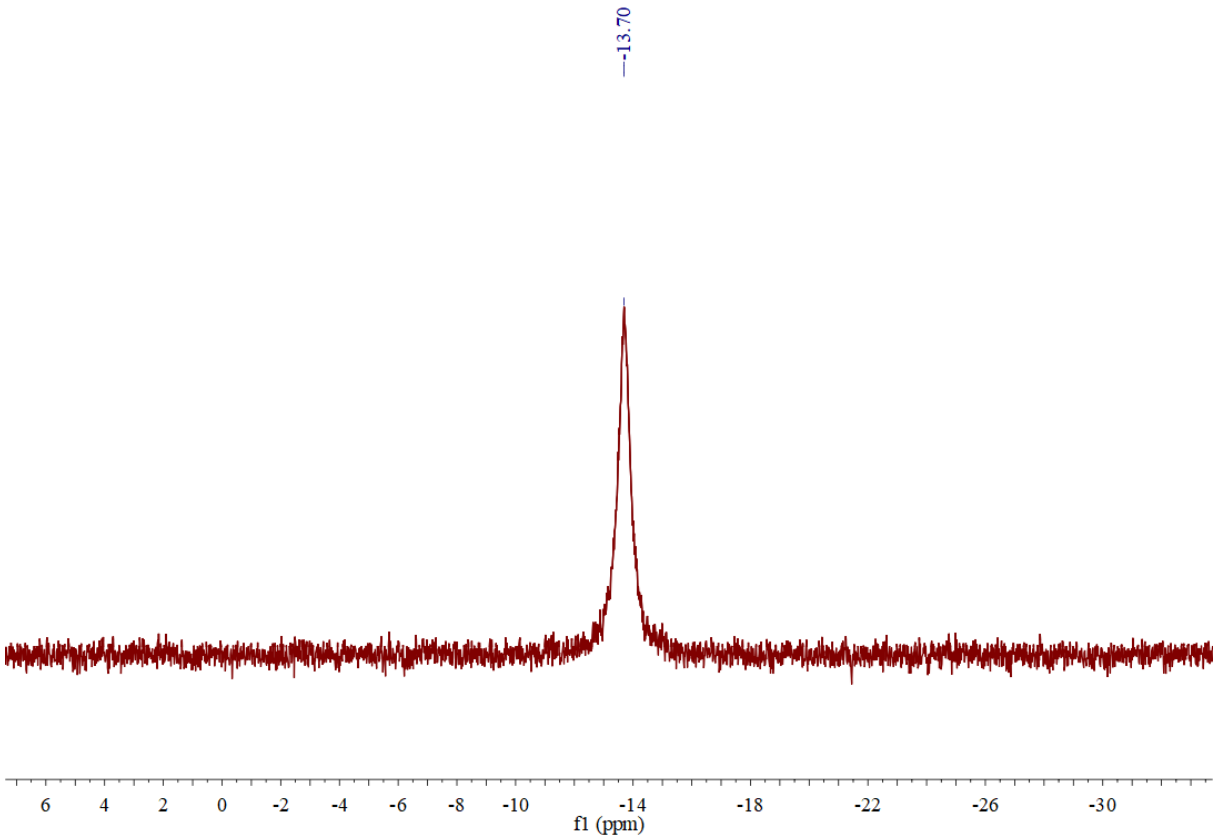

Fig. S3 ^{31}P NMR spectra of **1** in CD_2Cl_2.

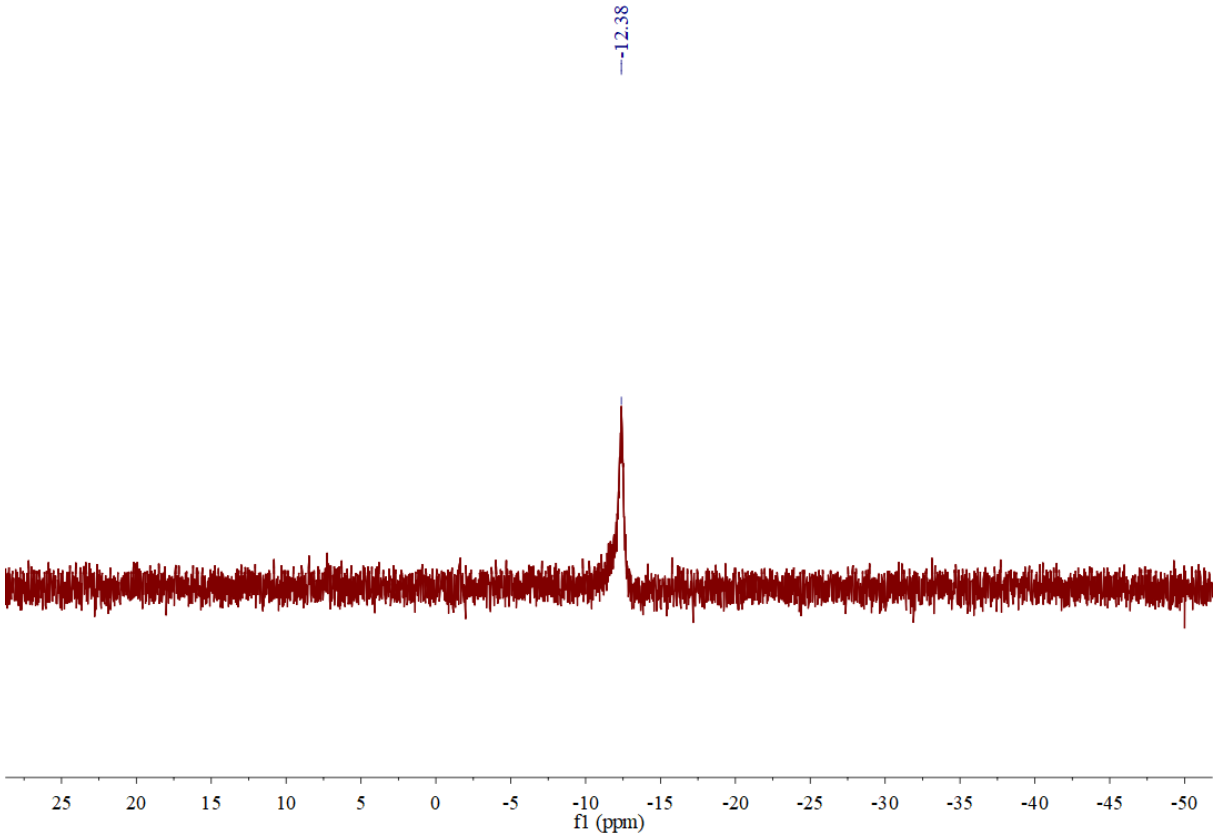

Fig. S4 ^{31}P NMR spectra of **2** in CD_2Cl_2.

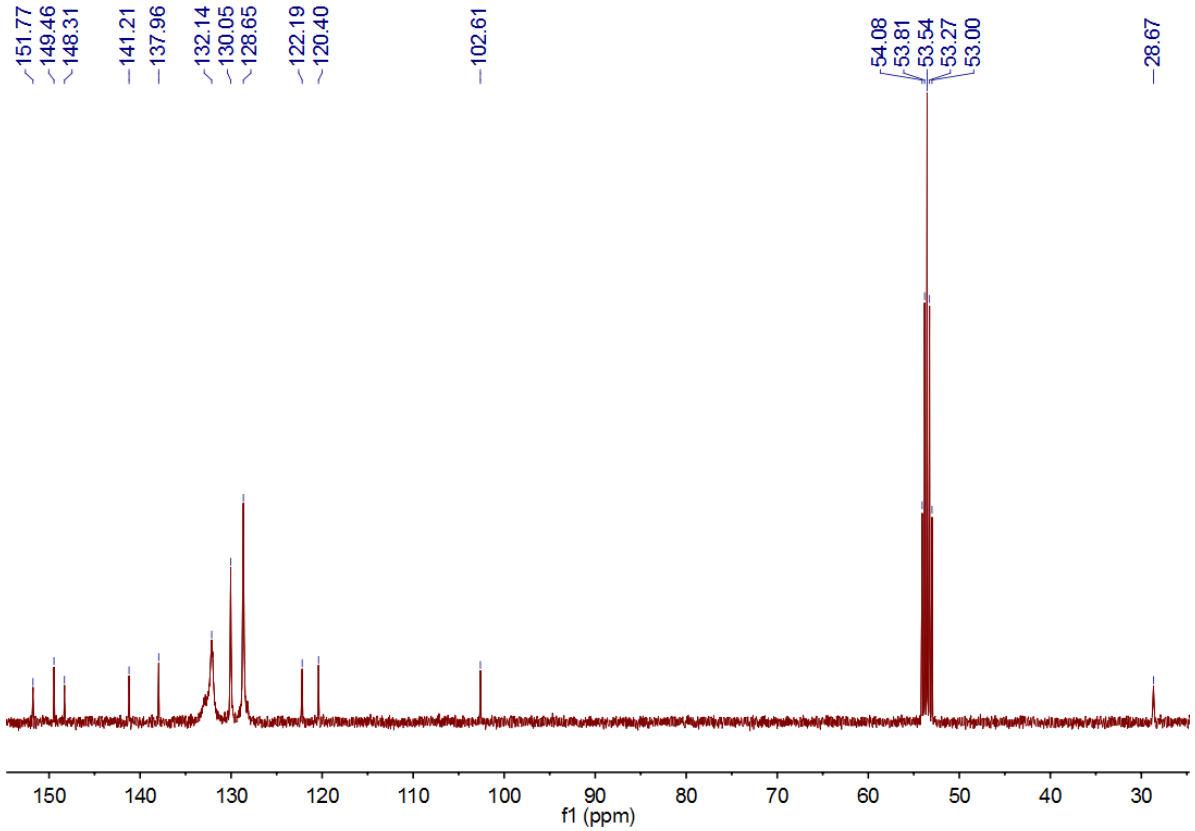

Fig. S5 ^{13}C NMR spectrum of **1** in CD_2Cl_2.

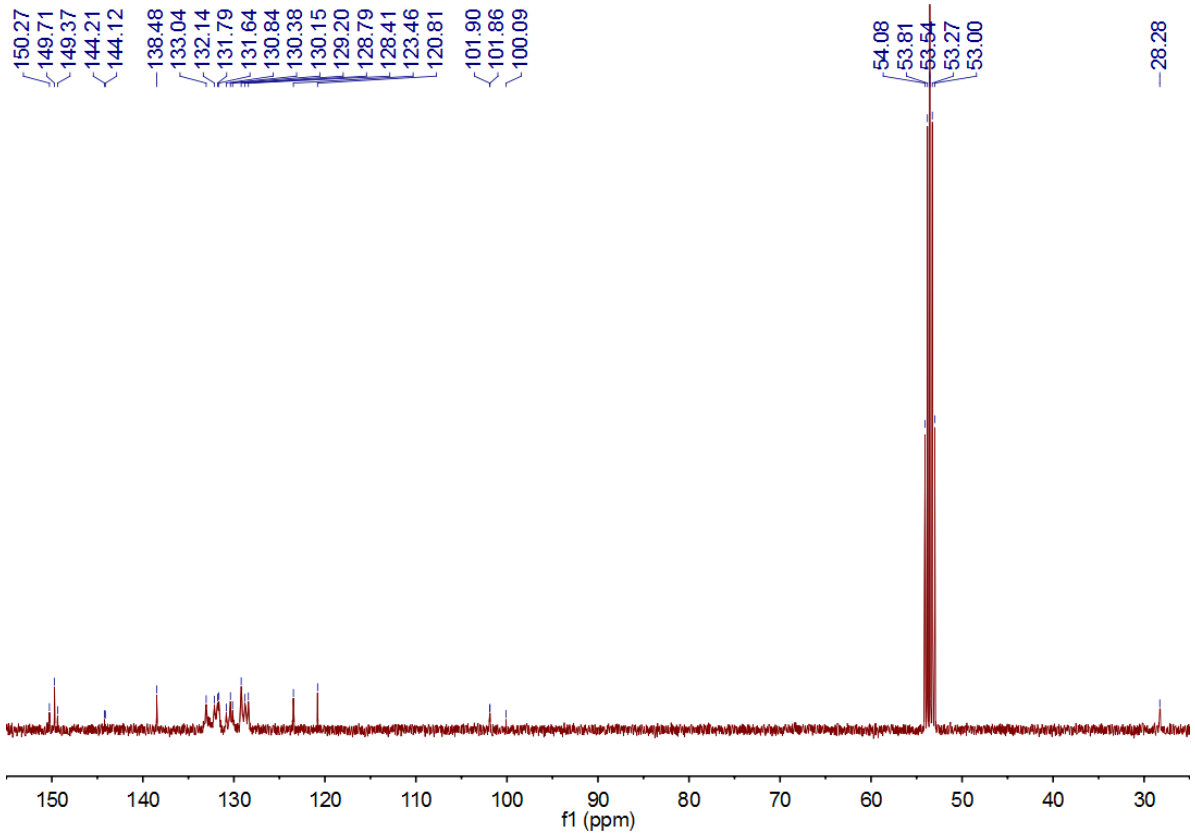

Fig. S6 ^{13}C NMR spectrum of **2** in CD_2Cl_2.

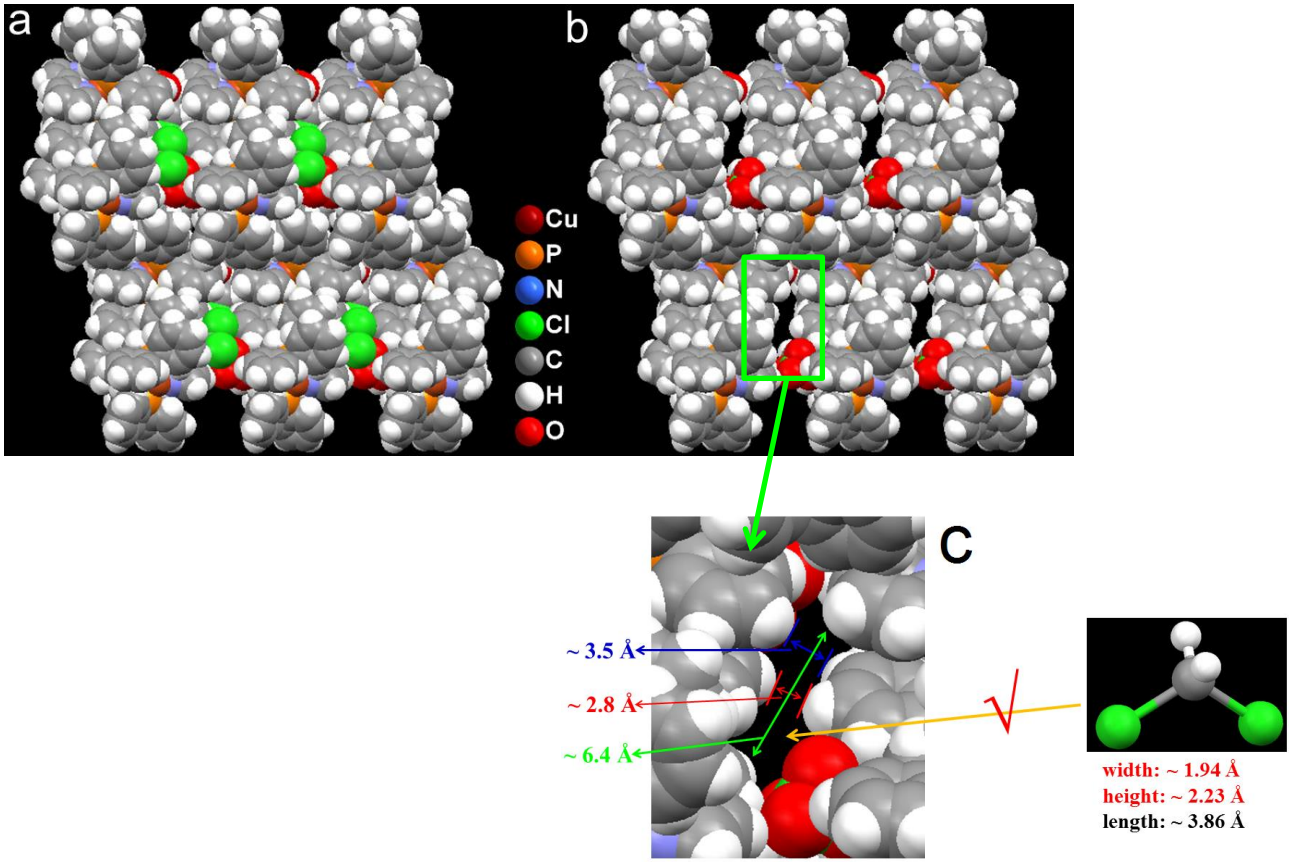

Fig. S7 Packing diagram of **1** along the *a* axis (a) with and (b) without CH_2Cl_2 solvate molecules; (c) the zoom of the window of the pore-channel structure of **1**.

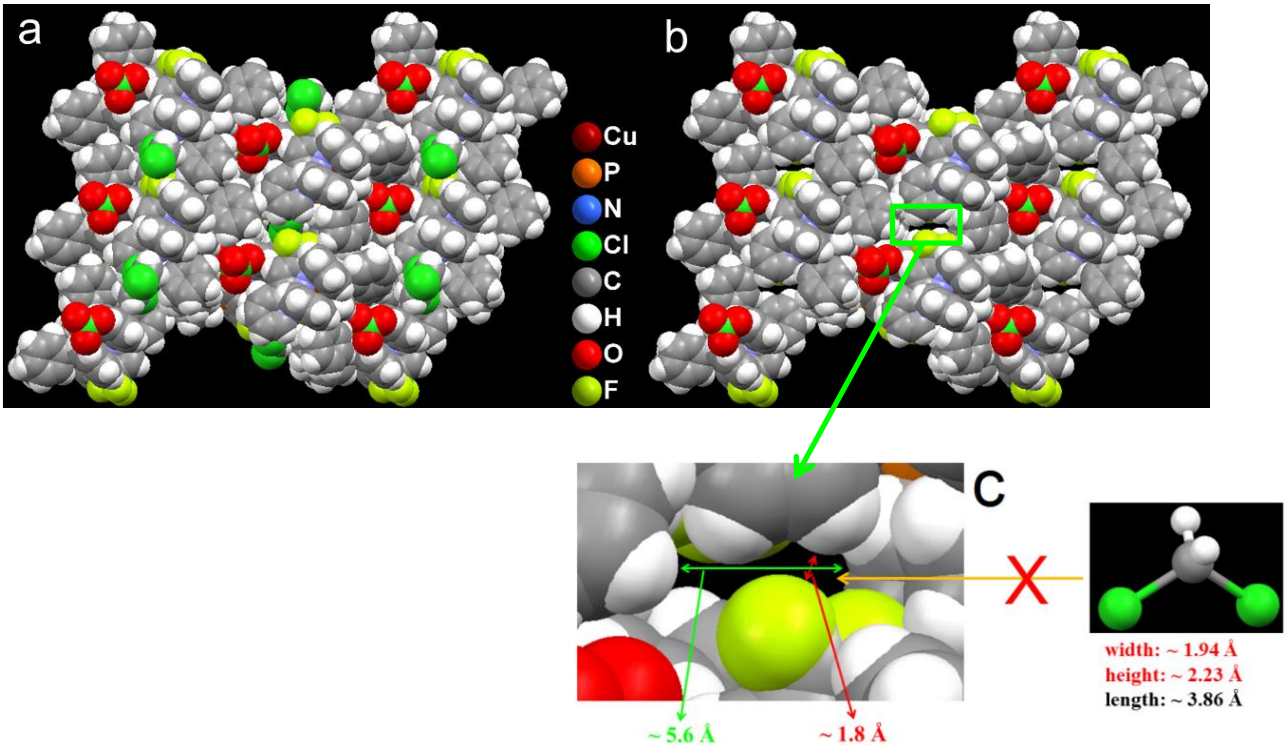

Fig. S8 Packing diagram of **2** along the *b* axis (a) with and (b) without CH_2Cl_2 solvate molecules; (c) the zoom of the window of the pore-channel structure of **2**.

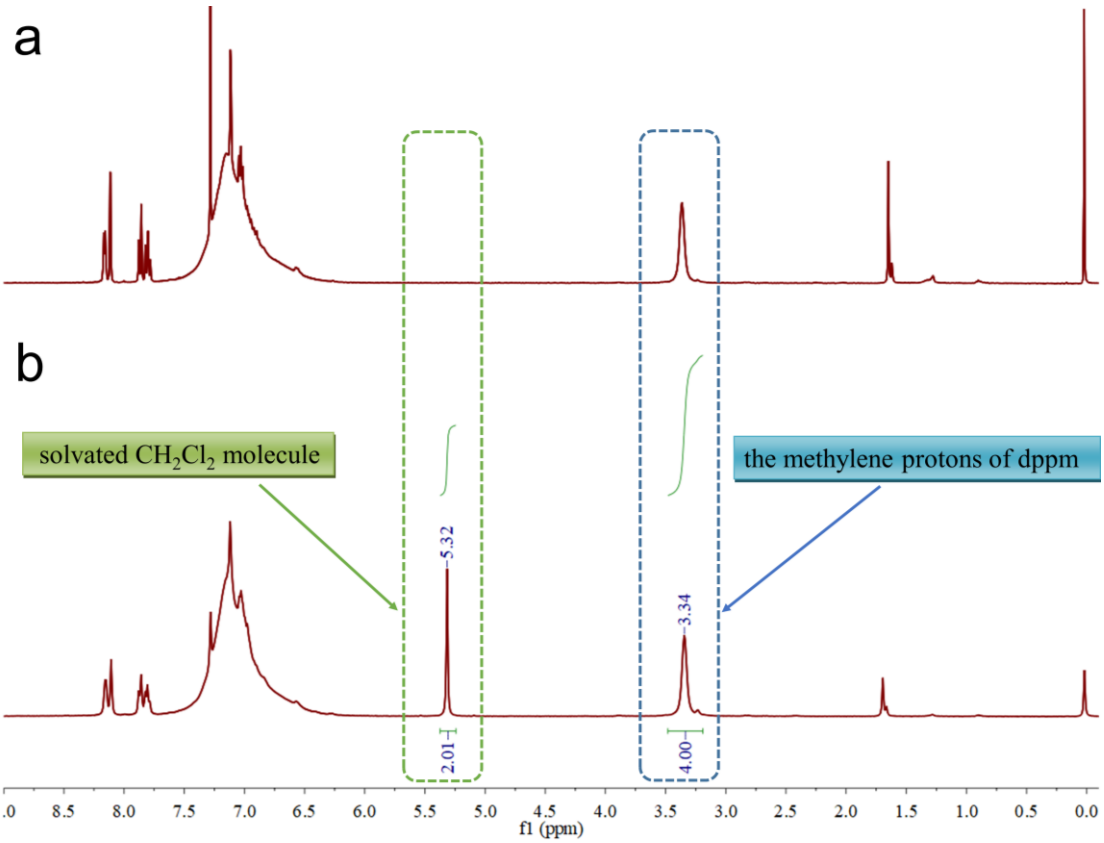

Fig. S9 ^{1}H NMR spectra of *desolvated* **1** (a) and *crystalline* **1** (b) in $CDCl_3$.

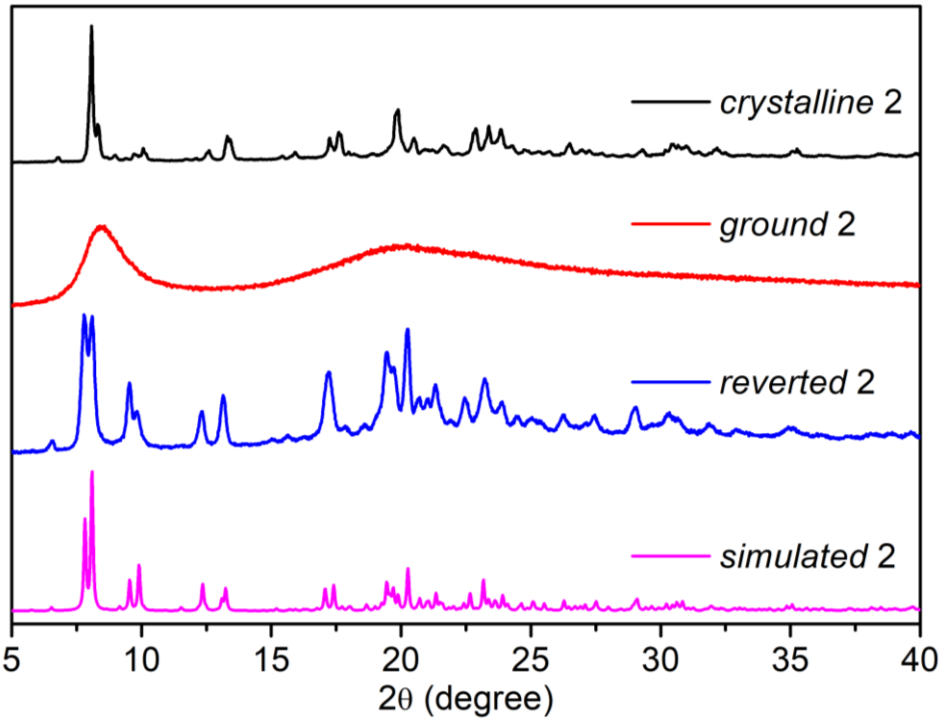

Fig. S10 PXRD patterns of the *crystalline*, *ground*, and *reverted* samples of **2** and that simulated from single-crystal data of **2**.

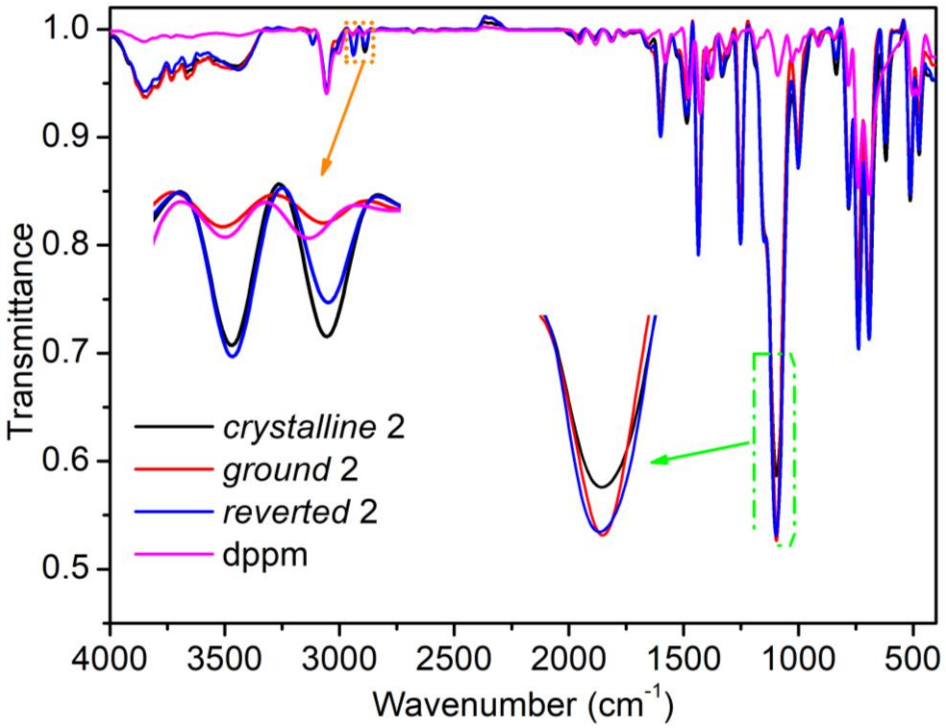

Fig. S11 FT-IR spectra of dppm and the *crystalline*, *ground*, and *reverted* samples of **2**. Inset: the zoom of the Cl−O and methylene C−H stretching vibration absorptions.

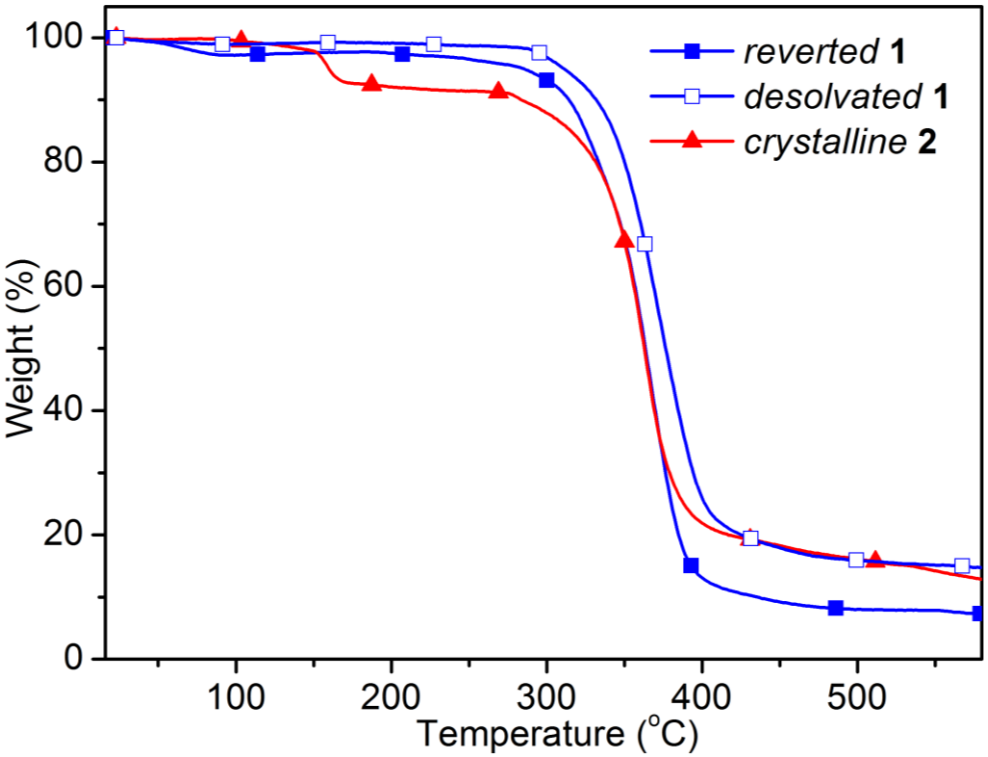

Fig. S12 TGA curves of *desolvated* **1**, *reverted* **1**, and *crystalline* **2**.

Table S1. Crystal data and structure refinement parameters of **1** and **2**

compound	**1**	**2**
formula	$C_{59}H_{52}Cl_3Cu_2N_3O_4P_4$	$C_{60}H_{51}Cl_3Cu_2F_3N_3O_4P_4$
fw	1224.34	1292.34
T (K)	293(2)	299(2)
crystal system	triclinic	Monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	12.9124(7)	11.7627(6)
b (Å)	14.3129(8)	18.5166(10)
c (Å)	17.8368(11)	27.2950(15)
α (deg)	71.683(2)	90
β (deg)	79.859(2)	98.1430(10)
γ (deg)	64.650(2)	90
V (Å^3)	2824.8(3)	5885.1(5)
Z	2	4
ρ_{calcd} (g cm^{-3})	1.439	1.459
μ (mm^{-1})	1.057	1.026
no. reflections collected	43308	101096
no. unique reflections	12857	13170
R_{int}	0.0327	0.0672
no. observed reflections	12857	13170
no. parameters	676	758
GOF on F^2	1.031	1.066
$R1$ [$I > 2\sigma(I)$]	0.0403	0.0553
$wR2$	0.0920	0.1032

Table S2. Selected Bond Lengths (Å) and Angles (deg) of **1** and **2**

compound	**1**	**2**
Cu1−N1	2.169(2)	2.189(3)
Cu1−N2	1.986(2)	2.017(3)
Cu1−P1	2.2514(7)	2.2613(10)
Cu1−P2	2.2462(7)	2.2454(10)
Cu2−N3	1.997(2)	2.032(3)
Cu2−P3	2.2310(7)	2.2426(10)
Cu2−P4	2.2426(7)	2.2432(10)
N1−Cu1−N2	78.56(9)	77.38(12)
N1−Cu1−P1	113.01(6)	111.86(8)
N1−Cu1−P2	114.68(6)	113.15(8)
N2−Cu1−P1	113.09(6)	113.59(8)
N2−Cu1−P2	118.84(7)	116.25(8)
P1−Cu1−P2	113.98(3)	117.86(4)
N3−Cu2−P3	116.26(7)	118.11(9)
N3−Cu2−P4	113.78(7)	117.47(9)
P3−Cu2−P4	127.50(3)	122.69(4)

Table S3. Photophysical Data of **1** and **2**

compound	medium	λ_{abs} [nm] (ε [M^{-1} cm^{-1}])	λ_{em} [nm]	τ [μs]	Φ_{em} [%]
1	CH_2Cl_2	276 (31467)	526	3	0.4
	solid		461,[a] 508,[c] 472[d]	210,[a] 48,[c] 185[d]	38,[a] 21,[c] 55[d]
2	CH_2Cl_2	275 (39030), 313 (14248)	527	6	1.1
	solid		492,[b] 506,[c] 493[d]	47,[b] 32,[c] 40[d]	88,[b] 28,[c] 81[d]

[a] *Desolvated* sample. [b] *Crystalline* sample. [c] *Ground* samples. [d] *Reverted* samples.